THE ACTION OF GASES ON MILD STEEL AT HIGH TEMPERATURE

BY

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1 9 1 6

CONTENTS

INTRODUCTION

When iron is heated to a temperature sufficiently high for welding or stamping operations, a film of iron oxide, Fe_3O_4, forms on the surface of the metal. In some cases this film of oxide is very thick resulting in the reduction in size of the material treated to such an extent that it must be discarded. In stamping operations where large quantities of iron are used the loss occasioned by discarded material presents a serious economic problem.

The main factors entering into the production of this scale are the duration of heating, the temperature and the composition of the gases surrounding the metal. If the formation of this scale is in the order of a simple chemical reaction, then the rate of formation would depend on the temperature time and rapidity with which oxygen is furnished to the reaction. In ordinary stamping operations the iron is brought to a welding temperature by means of coal gas or producer gas. In contact with the products of combustion of these gases the scale forms quite rapidly, so rapidly in fact as to present a serious obstacle to this method of heating. The rapid formation of scale may be due in a great part to the fact that considerable oxygen is available from the Co_2 which is reduced to Co or C, the oxygen entering with the air and that furnished by decomposed water vapor. The presence of moisture is known to play a very important part

in the formation of this scale.

As far as been able to determine no work has been done on the action of the products of combustion on iron at high temperatures. In this work an attempt was made to determine the relation between the amount of formation of this scale and the time temperature and composition of the gases surrounding the metal, and further to determine the most suitable conditions of time, temperature and composition of gases for carrying on stamping and welding operations. This being the first work in the field it must be taken simply for what it may be worth in suggesting further work along this line.

This work was suggested by C. W. Zachow, a former graduate of this University, who at present is connected with work of this kind.

PICKLING

At the outset it was seen that the success of this work depended on being able to pickle the samples treated without further corrosion due to the action of the pickling bath. It was also desirable to have some method by which the pickling could be rapidly carried on. Reed's electrolytic method seems to fulfill these requirements. In some experiments performed in the electro-chemical laboratory by students it was found that excessive corrosion occurred when this method was used, but it was thought that the corrosion

was due to the acid itself and not to electro-chemical causes. If this were the case it was evident that Reed's method could not be used. Further experiments showed that by raising the current density to between 1200 and 1500 amperes per square foot that this method gave the desired results and that a specimen covered with a heavy coating of scale could be cleaned in thirty seconds. A number of tests were run to find if any corrosion resulted from the action of the bath and it was found that the corrosion due to such action was less than one hundredth of one per cent. It was then by this, Reed's method with increased current density that all of the pickling was done.

The apparatus arranged for this work was as follows:- A small iron bucket five inches in diameter and five inches deep covered with acid resistant enamel was fitted with two lead anodes 3½ inches by 5 inches, placed one on either side. A heavy copper wire bared at the end for contact was extended nearly to the center of the bucket in the plane of the top. On this wire a screw pinch-cock holding the specimen could be hung. The specimen could be easily and quickly changed. The pinch-cock made very good contact with the copper and heavy sparks occurred only at making and breaking the contact. Sulphuric acid Sp. Gr. 1.27 was used as electrolyte. A thermometer was inserted in the bath which was raised to $65^{\circ}C$ by a bunsen flame and maintained at that temperature by the passage of the current. An ammeter was

connected in the circuit to show whether the current passing was sufficient for the required current density of 1200 to 1500 amperes per square foot. In this connection it should be stated that when this bath is used at this high current density the operations should be carried on in a hood, for with the rapid evolution of hydrogen a spray of sulphuric acid is carried into the air. A number of slight explosions occurred in the use of this bath at the instant of the removal of the specimen, the evolved hydrogen being ignited by a spark from the broken contact. The arrangment of this apparatus can be seen somewhat in detail from the cut in Plate II.

FURNACE

The furnace used was designed and built solely for this work. Among the requirements of the furnace were:-

a. Maintenance of uniform temperatures.

b. Capacity for variation of temperature from 800°C to 1200°C.

c. Facilities for accurate measurement of temperatures.

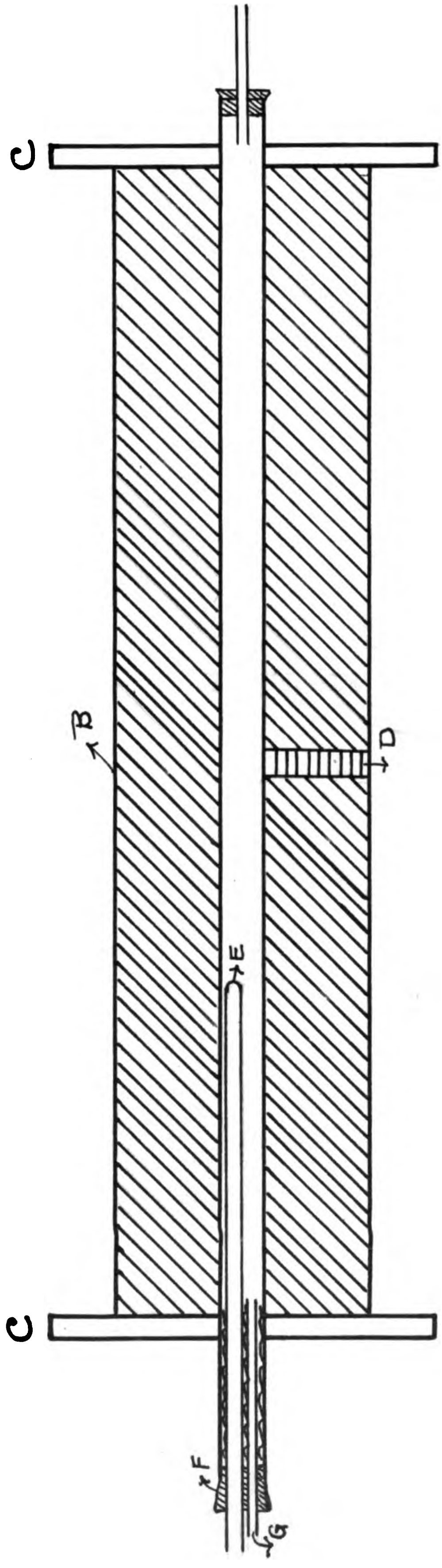
d. Capacity to heat the gases to the required temperature before they come in contact with the specimens.

e. Facilities for admitting gas to the furnace and rendering the furnace air tight.

The furnace as designed and built is shown in Fig. 1. It consists of an electric tube furnace wound with Nichrome wire designed for use on a 220 volt circuit. Since

FIGURE I

FIGURE I



the temperature attained is dependent on the current flowing, to maintain constant temperatures it is necessary only to control the current flowing in the heating unit. This was done by a choke coil shown in Plate IV.

Fig. 1 shows a cross sectional view of the tube furnace. A is a heavy porcelain tube 1½ inches in diameter and 46 inches in length wound with twenty feet of Nichrome wire. B is a tubular galvanised iron shield seven inches in diameter and thirty-six inches in length which is bolted to eleven inch squares of asbestos board C, each one-fourth inches in thickness. The intervening space is filled with fossil flour loosely packed.At the center is placed an asbestos support D to prevent the tube from sagging at high temperatures. E is a silica tube closed at one end and extending twelve inches into the interior of the heated region of the furnace and in this tube was placed a thermo-couple or the tube was used as a "black body" when measurement of temperature was made by optical means. G is a small silica tube bearing the gases to the furnace and delivering them directly under tube E. The gases rising around E would have a tendency to cool it and if the tube were maintained at the desired temperature it would mean that the gases were raised to that temperature before they came in contact with the specimens. As is shown in Fig. 1 the porcelain tube extends beyond the frame of the furnace for a distance of about eight inches and is closed by a rubber stopper F

thru which the two silica tubes E and G pass. Between the rubber stopper and the point where the porcelain tube enters the furnace the silica tubes are surrounded by a layer of asbestos which protects the stopper from the heat conducted and radiated from the interior. While runs were made at 1200°C and the furnace maintained at this temperature for a half hour and longer, the end of the tube remained perfectly cool. The right end of the furnace was closed by a small glass tube one-eight inch inside diameter wound with asbestos cord. The small opening was needed to allow the passage of gas out of the furnace.

The winding of the furnace was very uniform and as a result the temperature remained uniform throughout its length. This was shown by inserting a thermo-couple in various parts of the furnace. The gas was passed thru the furnace at a uniform rate of one hundred cubic inches per minute, the flow being regulated by a wet meter.

The temperature of the furnace was at first measured by placing a base metal thermo-couple in the silica tube E. This worked well except for 1100 and 1200°C. At these temperatures particularly the latter the thermo-couple did not stand well. The use of the thermo-couple was abandoned and a Holborn-Kurlbaum optical pyrometer with silica tube E as "black body" was used. This method was very satisfactory and was used for the greater part of the work.

PREPARATION OF GASES

The gases used were made up in a gas holder of six cubic feet capacity. The nitrogen was obtained by passing compressed air thru an absorbing system containing alkaline pyrogallol. The system is shown in Plate II. It consists of a train of four suction filter flasks of two and one half liters capacity each, each containing one and one fourth liters of alkaline pyrogallol, and a small filter flask containing water only. The alkaline pyrogallol was made by adding fifty grams of pyrogallic acid per liter of twenty-five per cent. solution of potassium hydroxide. On the end of each glass tube leading down into the pyrogallate was placed a rubber stopper over which a layer of glass wool was placed and secured with a cotton cloth. With this arrangement air forced thru the tube came to the surface of the pyrogallate as a spray of fine bubbles presenting a large surface for the absorption oxygen. Very pure nitrogen was obtained in this way when air was passed thru at the rate of three cubic feet per hour.

The carbon dioxide was supplied in pressure cylinders and was drawn out thru a reducing valve as was needed. The gas was made up by volume. A small amount of air, the same amount each time, was entrapped in the tank. This furnished four per cent. of oxygen. The composition of the gas was repeatedly checked by a Hempel Burette. The tank was loaded with lead sufficient to give a gas pressure

of seven inches of water. The gas in passage from the tank to the furnace passed first thru the wet meter where it was regulated, then to the saturator or dryer as the case might be, and thence into the furnace. The saturation of the gas with water vapor was accomplished by passing it thru saturated excelsor , the drying by a calcium chloride tower.

SPECIMENS

The specimens were of mild steel $3\frac{1}{4}$" x $\frac{1}{2}$" x $\frac{1}{4}$" and weighed approximately fifty grams each. They were run in sets of five and marked by punch marks, each marked specimen denoting the time for which it was treated. The marking was as follows:-

No mark - - - - - -	5 minutes
1 Punch mark - - - --	10 "
2 " " - - - -	15 "
3 " " - - - - -	20 "
4 " " - - - -	30 "

With this system of marking there was little if any chance of confusing the specimens.

METHOD

The work was carried on in sets or "runs". Each "run" consisted in the treatment of twenty-five specimens with gas of the same composition, but at different temperatures and different lengths of time. Five different temperatures were used, viz., 800°, 900°, 1000°, 1100°and 1200°C. At each temperature five samples were treated for 5, 10, 15, 20 and 30 minutes.

The specimens were first pickled for thirty seconds to remove any scale, dipped in a water solution of sodium carbonate to neutralize the acid from the bath and then in an alcoholic solution of sodium carbonate to facilitate rapid drying and to prevent any oxidation due to exposure in the air. The specimens were then weighed, placed in porcelain boats and slided into the furnace which was at the desired temperature. In each case two minutes was allowed before time was counted to bring the specimens up to the temperature of the furnace. A sample was removed at the end of 5,10, 15, 20 and 30 minutes periods. The porcelain boats were used for convenience in getting the specimens in and out of the furnace, and also, to prevent the specimens from fluxing with the porcelain tube at high temperatures. The specimens on removal from the furnace were cooled, pickled in the usual manner and weighed. The loss of weight was taken as the amount of oxidation due to the action of the gas. Time-oxidation and temperature-oxidation curves were plotted for each run.

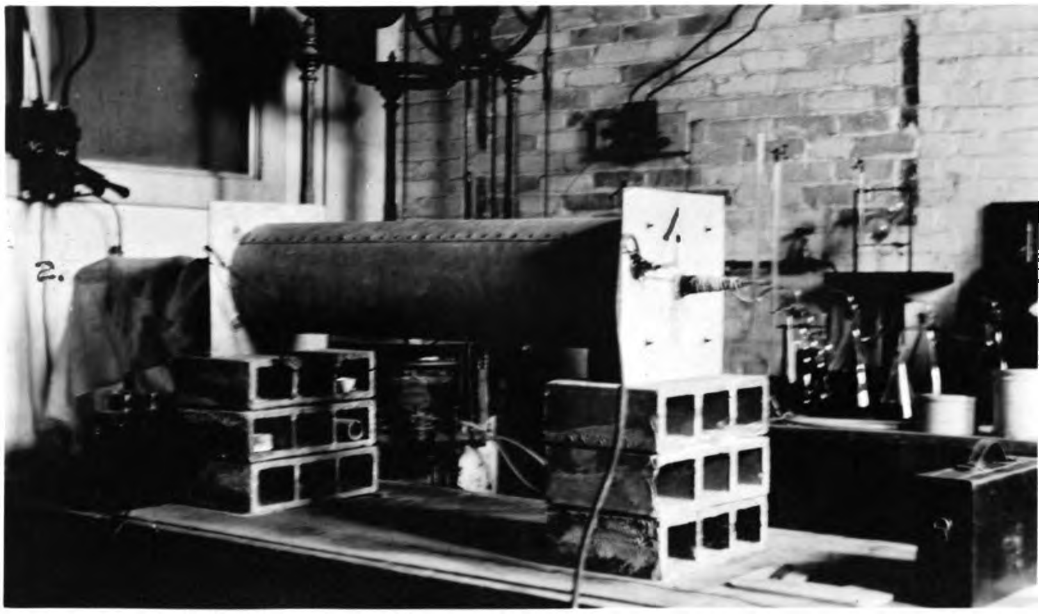


PLATE I

1 SHOWING FURNACE IN POSITION

2 PYROMETER

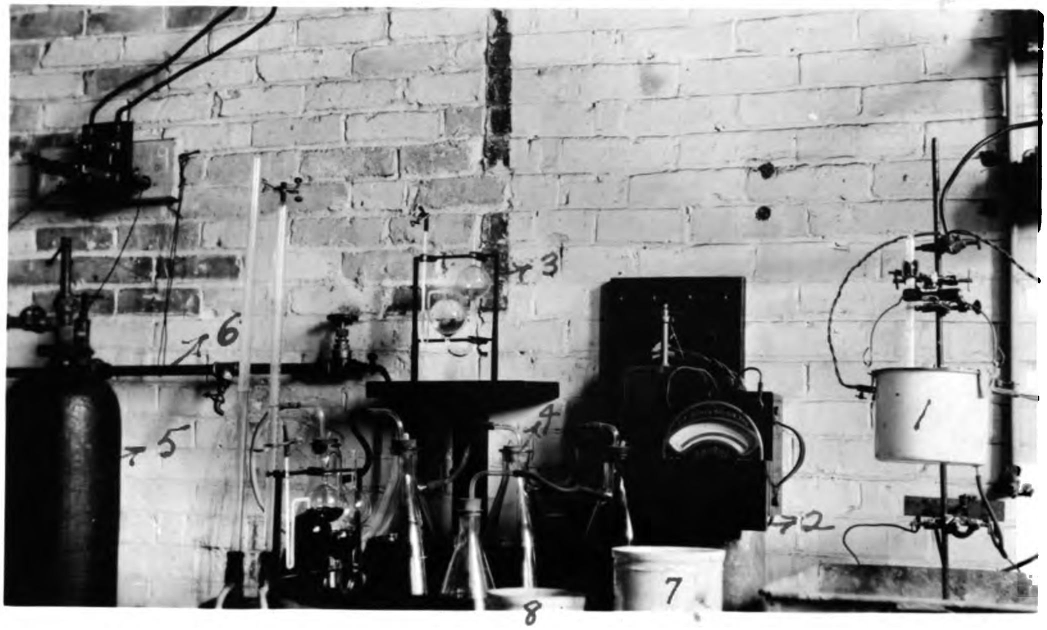


PLATE II

1-Pickling Bath

2-Ammeter connected to bath

3-Hempel Apparatus

4-Absorption train

5-CO_2 Cylinder

6-Compressed air Piping

7-Solution of Na_2CO_3.

8-Alcoholic Na_2CO_3

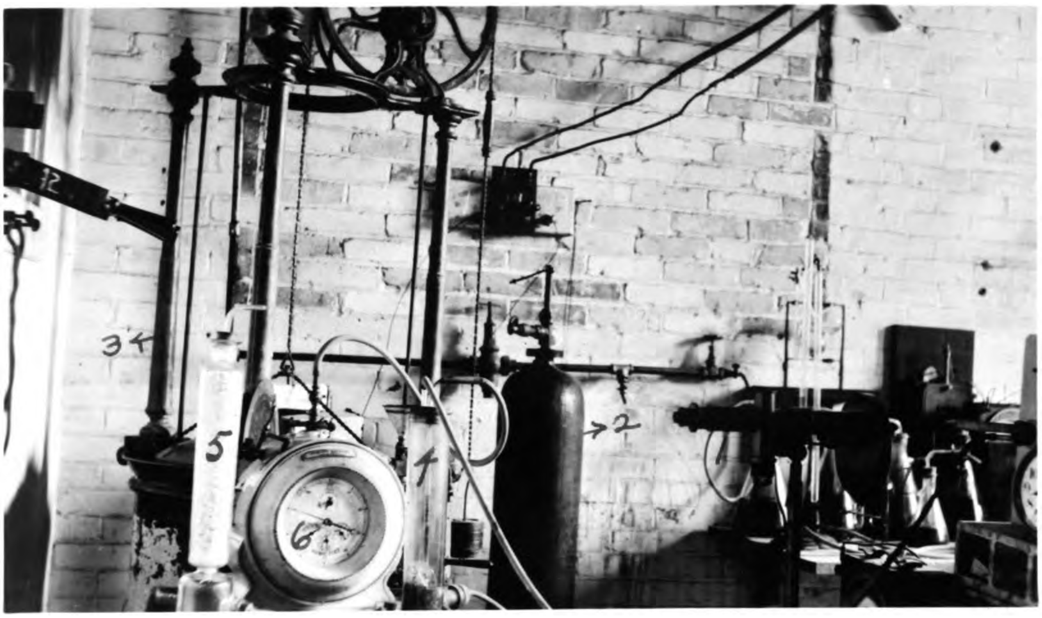


PLATE III

1-Holborn-Kurlbaum Pyrometer.

2-CO_2 Cylinder.

3-Gas holder.

4-Gas Saturator.

5-Calcium chloride tower.

6-Wet gas meter.

PLATE IV

SHOWING CHOKE COIL USED IN REGULATING THE CURRENT IN THE FURNACE

TABLE NO I

(Run No I)

GAS SATURATED WITH WATER VAPOR

Composition of Gas

Co_2 10%--O_2 4%

N_2 86%

TEMPERATURE DEGREES C.	Time Min. 5	Time Min. 10	Time Min. 15	Time Min. 20	Time Min. 30
	% Oxidation	% Oxidation	% Oxidation	% Oxidation	% Oxidation
800	0.61	0.65	0.74	1.25	3.30
900	0.08	0.16	0.47	0.91	2.72
1000	0.77	2.11	3.53	4.45	5.71
1100	0.56	1.64	2.66	3.72	7.88
1200	0.23	0.59	0.88	3.11	11.10

TABLE NO II

(Run No II)

GAS SATURATED WITH WATER VAPOR

Composition of Gas

Co_2 15%--O_2 4%

N_2 81%

Temperature Degrees C	Time Min. 5	Time Min. 10	Time Min. 15	Time Min. 20	Time Min. 30
	% Oxidation	% Oxidation	% Oxidation	% Oxidation	% Oxidation
800	0.31	0.69	1.32	1.48	3.26
900	0.346	0.40	1.61	2.05	4.95
1000	0.25	0.76	1.00	4.25	6.00
1100	0.29	0.45	0.50	3.18	8.80
1200	0.40	0.63	1.82	5.87	12.80

TABLE NO III

(Run No III)

GAS SATURATED WITH WATER VAPOR

Composition of Gas

CO_2 20%--O_2 4%

N_2 76%

Temperature Degrees C	Time Min. 5	Time Min. 10	Time Min. 15	Time Min. 20	Time Min. 30
	% Oxidation	% Oxidation	% Oxidation	% Oxidation	% Oxidation
800	0.30	0.50	0.92	1.06	1.55
900	0.39	0.61	1.09	1.28	1.78
1000	0.35	0.53	1.53	3.77	5.60
1100	0.36	0.86	1.12	3.91	8.12
1200	0.68	0.98	1.48	3.50	11.50

TABLE NO IV

(Run No IV)

GAS DRY

Composition of Gas

Co_2 10%--O_2 4%

N_2 86%

Temperature Degrees C	Time Min. 5	Time Min. 10	Time Min. 15	Time Min. 20	Time Min. 30
	% Oxidation	% Oxidation	% Oxidation	% Oxidation	% Oxidation
800	0.34	0.67	1.35	1.84	2.90
900	0.26	0.54	1.35	2.36	3.50
1000	0.30	0.66	1.14	2.56	5.55
1100	0.47	0.71	0.83	2.84	11.60
1200	0.83	0.50	0.79	1.66	14.40

TABLE NO V

(Run No V)

GAS DRY

Composition of Gas

Co_2 15%--O_2 4%

N_2 81%

Temperature Degrees C	Time Min. 5	Time Min. 10	Time Min. 15	Time Min. 20	Time Min. 30
	% Oxidation	% Oxidation	% Oxidation	% Oxidation	% Oxidation
800	0.13	0.34	0.42	0.68	1.92
900	0.17	0.31	0.45	0.95	2.58
1000	0.26	0.48	0.79	1.43	4.45
1100	0.63	0.65	1.02	1.63	6.10
1200	0.46	0.67	0.84	1.84	8.40

TABLE NO VI

(Run No VI)

GAS DRY

Composition of Gas

Co_2 20%--O_2 4%

N_2 76 %

Temperature Degrees C	Time Min. 5	Time Min. 10	Time Min. 15	Time Min. 20	Time Min. 30
	% Oxidation	% Oxidation	% Oxidation	% Oxidation	% Oxidation
800	0.18	0.30	0.32	0.63	1.71
900	0.13	0.22	0.40	0.53	2.62
1000	0.44	0.62	0.94	1.87	5.21
1100	0.45	0.67	0.66	2.01	5.30
1200	0.82	1.34	1.56	2.22	5.35

TABLE NO VII

(Run No VII)

GAS SATURATED WITH WATER VAPOR

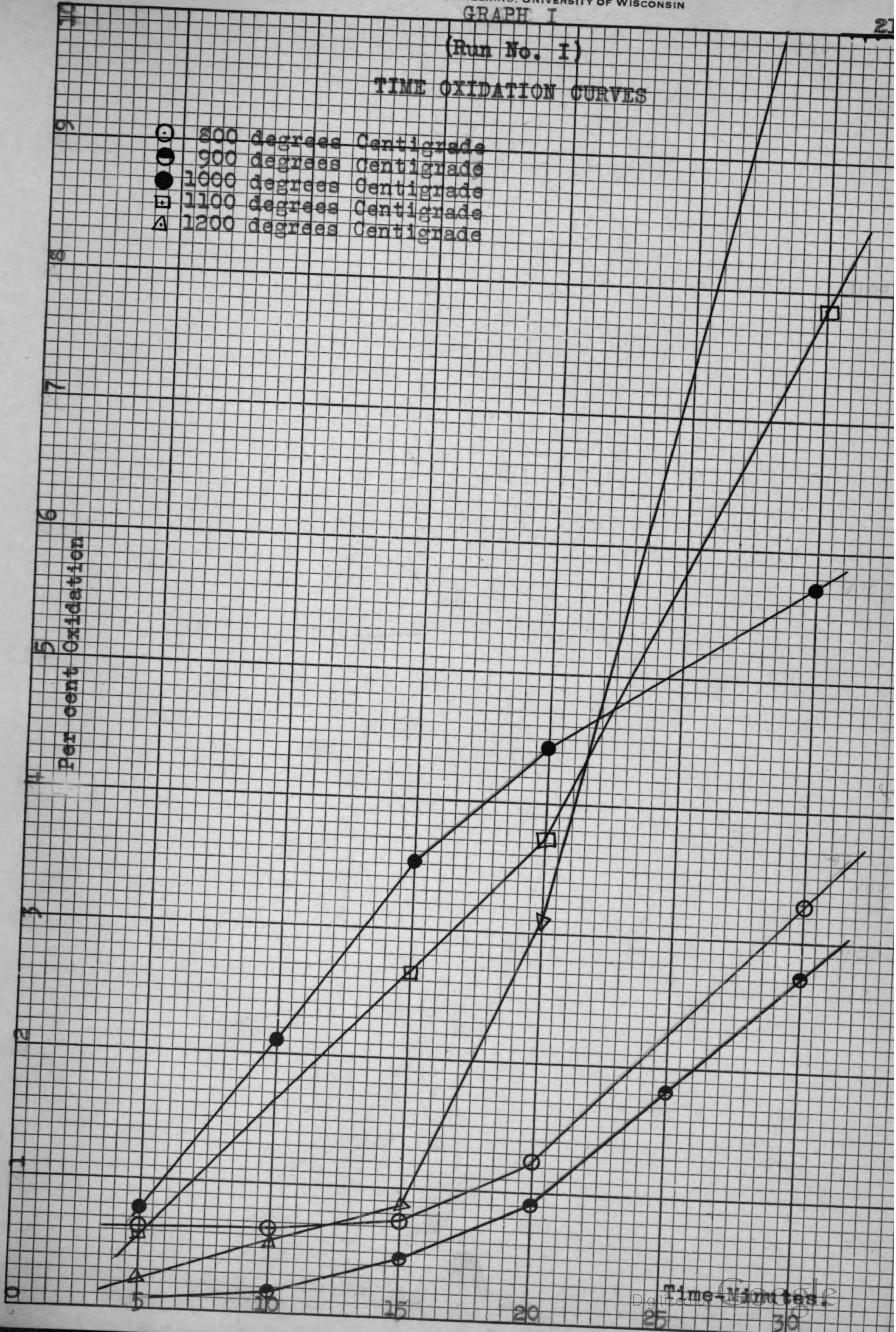
Composition of Gas

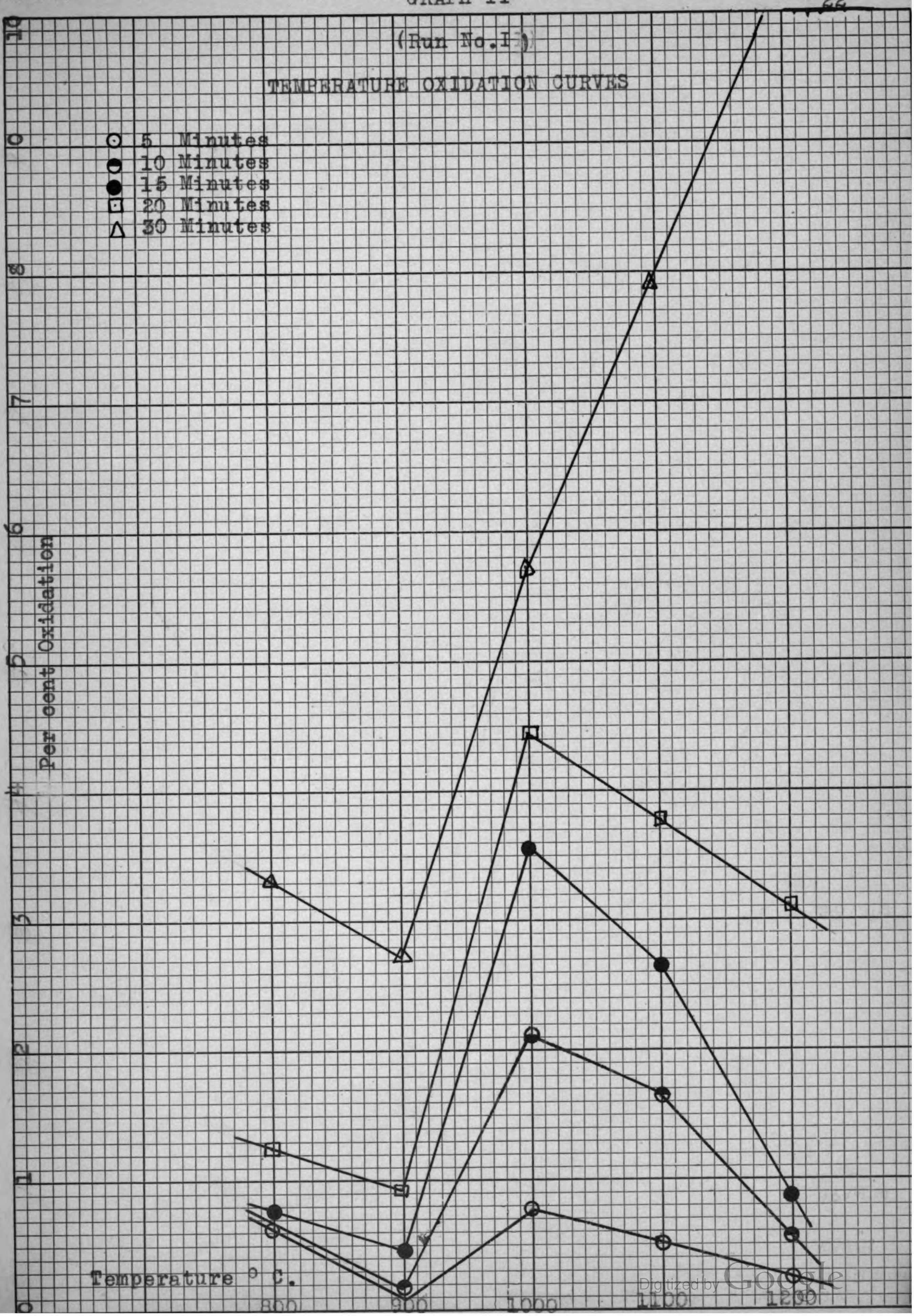
Co_2 10%--N_2 40%

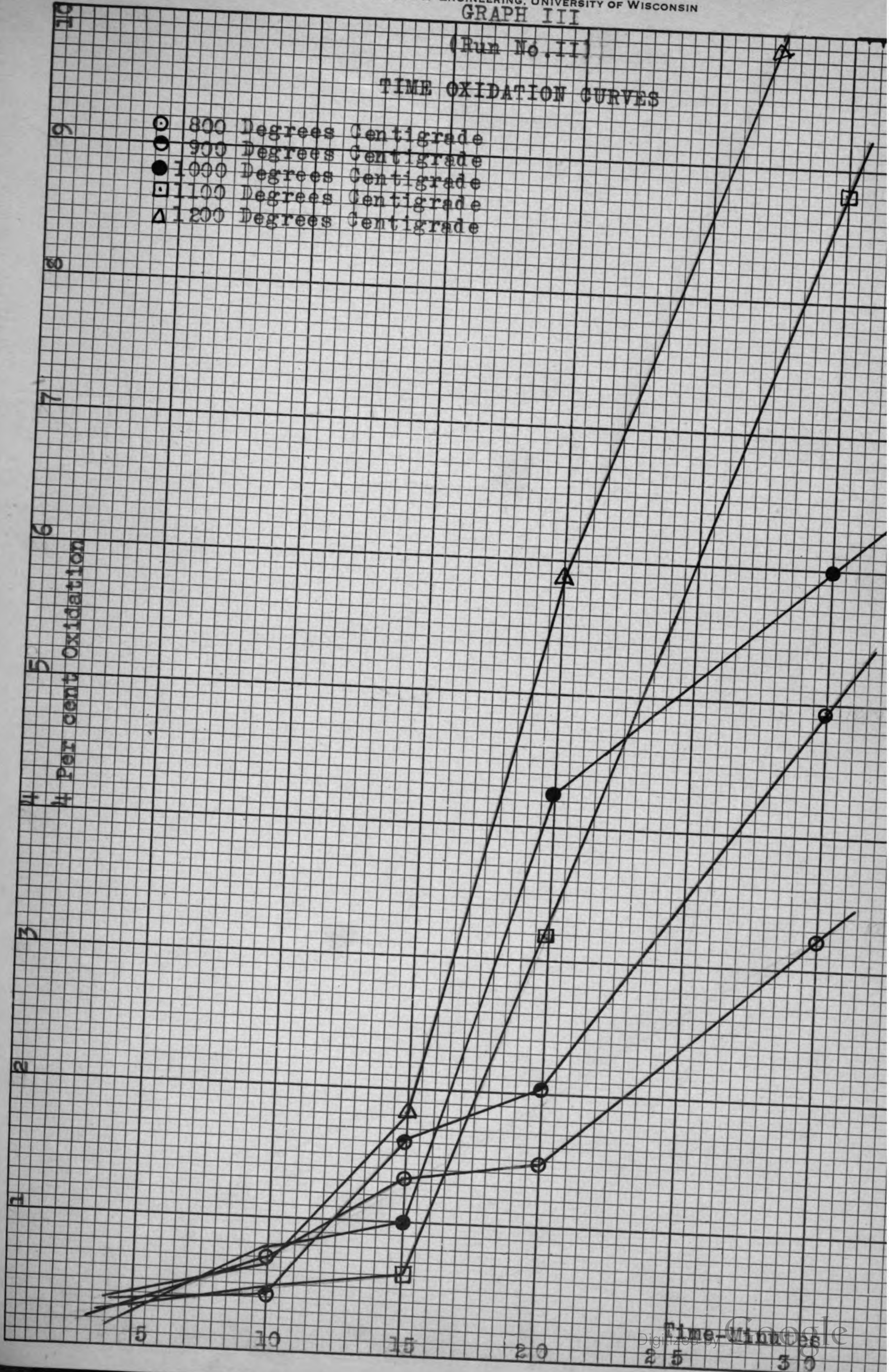
Cur 50%

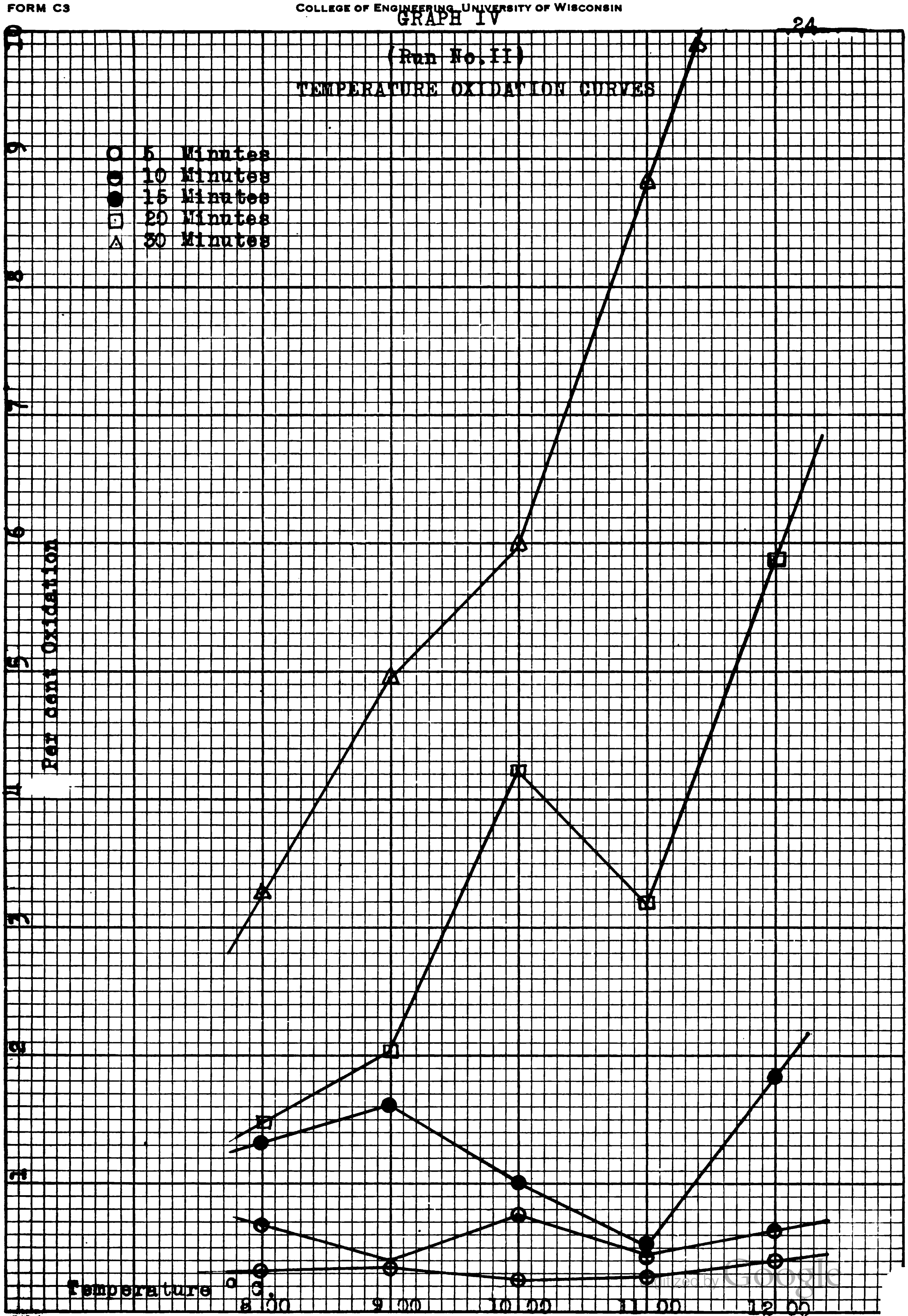
Temperature Degrees C	Time Min. 5	Time Min. 10	Time Min. 15	Time Min. 20	Time Min. 30
	% Oxidation	% Oxidation	% Oxidation	% Oxidation	% Oxidation
800	0.23	0.42	0.48	0.67	1.15
900	0.25	0.37	0.59	0.68	1.08
1000	0.44	0.62	0.71	1.12	1.75
1100	0.12	0.69	1.99	2.45	5.05
1200	0.76	0.94	1.88	4.58	10.00

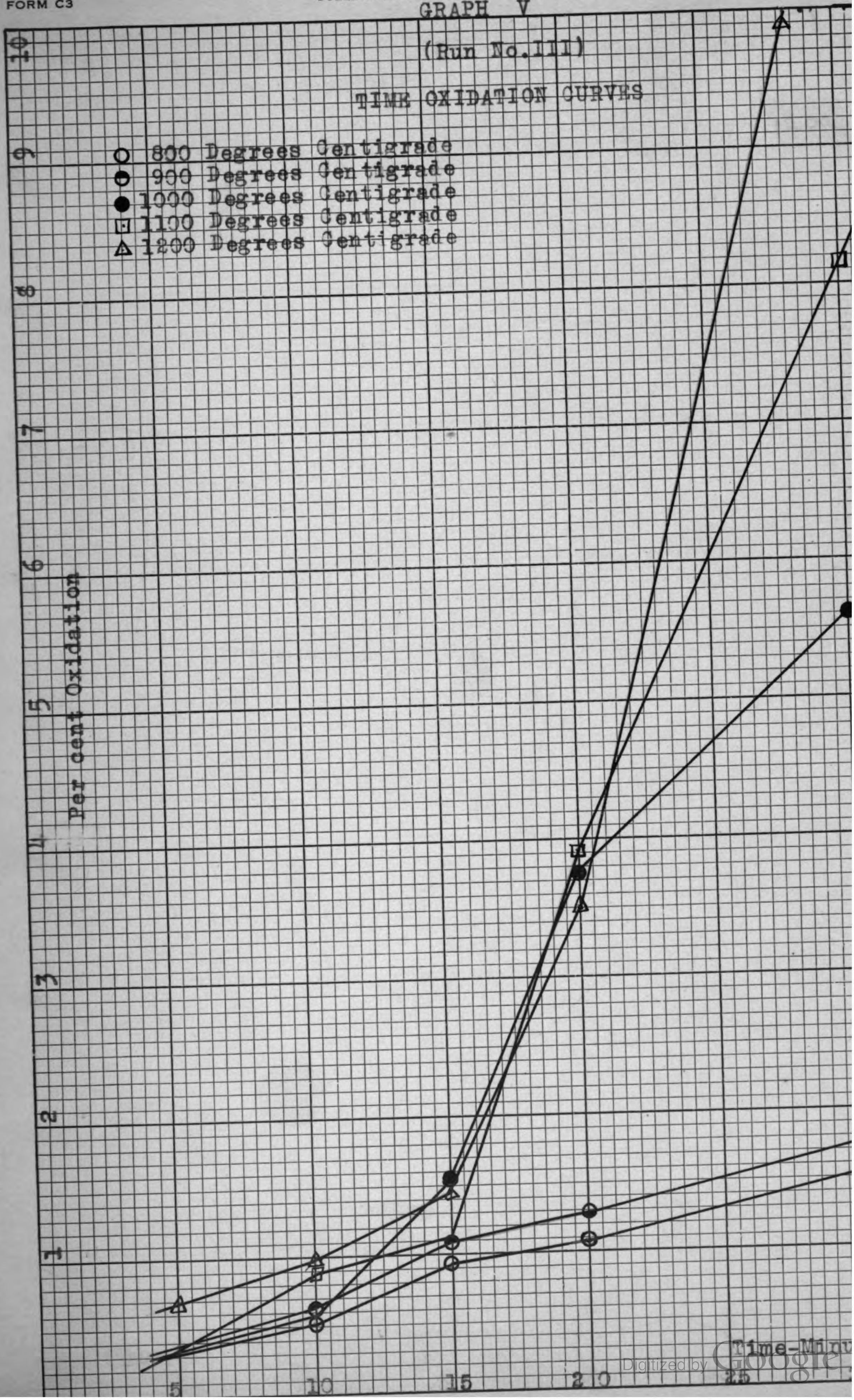
FORM C3

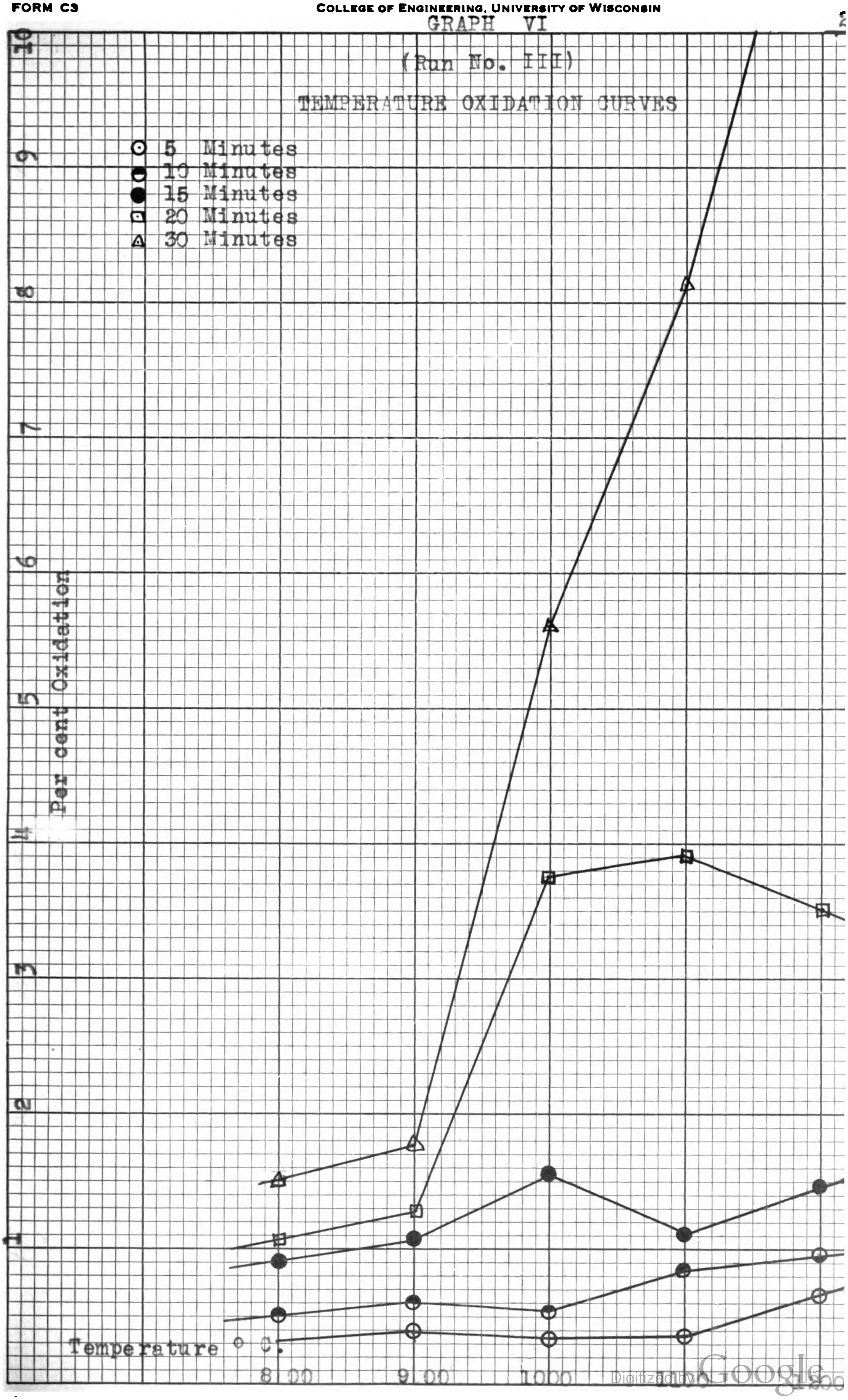

GRAPH I
(Run No. I)
TIME OXIDATION CURVES
800 degrees Centigrade
900 degrees Centigrade
1000 degrees Centigrade
1100 degrees Centigrade
1200 degrees Centigrade
Per cent Oxidation
Time-Minutes.
0
1
2
3
4
5
6
7
8
9
10
5
10
15
20
25
30

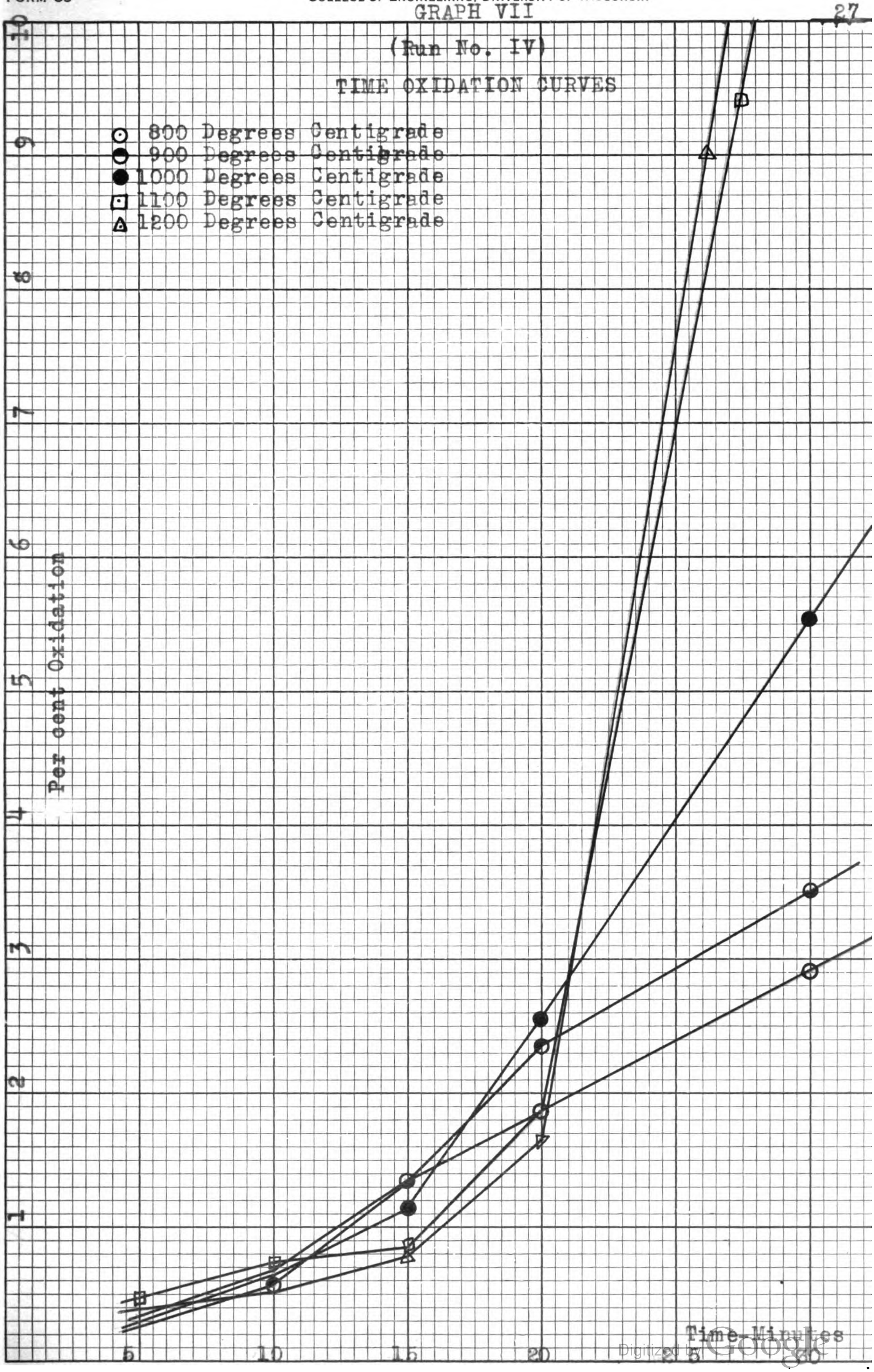

GRAPH II
(Run No.I)
TEMPERATURE OXIDATION CURVES
5 Minutes
10 Minutes
15 Minutes
20 Minutes
30 Minutes
Per cent Oxidation
Temperature ° C.
0
1
2
3
4
5
6
7
8
9
10
800
900
1000
1100
1200

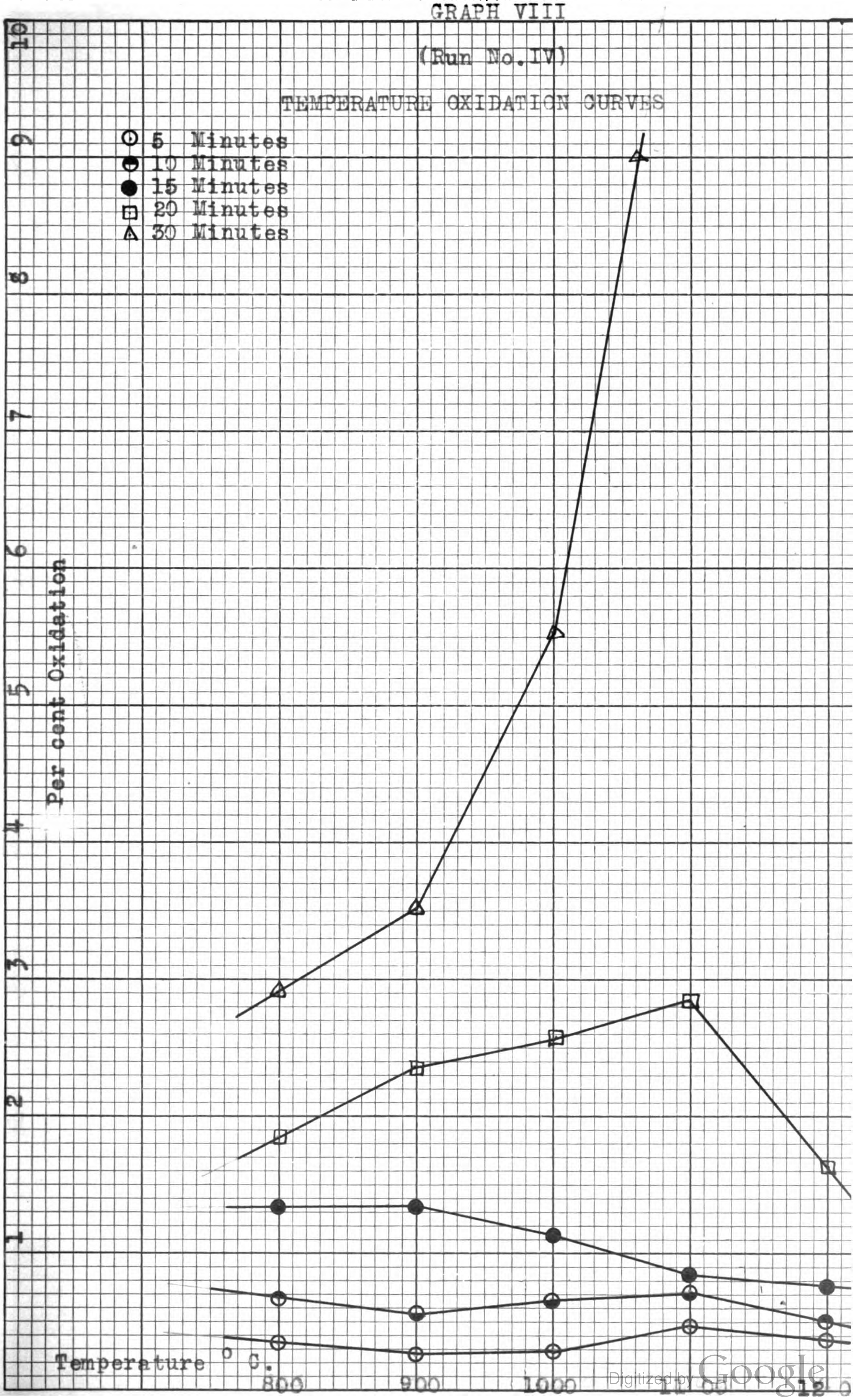

GRAPH III
(Run No.II)
TIME OXIDATION CURVES
800 Degrees Centigrade
900 Degrees Centigrade
1000 Degrees Centigrade
1100 Degrees Centigrade
1200 Degrees Centigrade
Per cent Oxidation
1
2
3
4
5
6
7
8
9
10
5
10
15
20
25
30
Time-Minutes


GRAPH IV
(Run No. II)
TEMPERATURE OXIDATION CURVES
5 Minutes
10 Minutes
15 Minutes
20 Minutes
30 Minutes
Per cent Oxidation
Temperature °C.
8.00
9.00
10.00
11.00
12.00
10
9
8
7
6
5
4
3
2
1

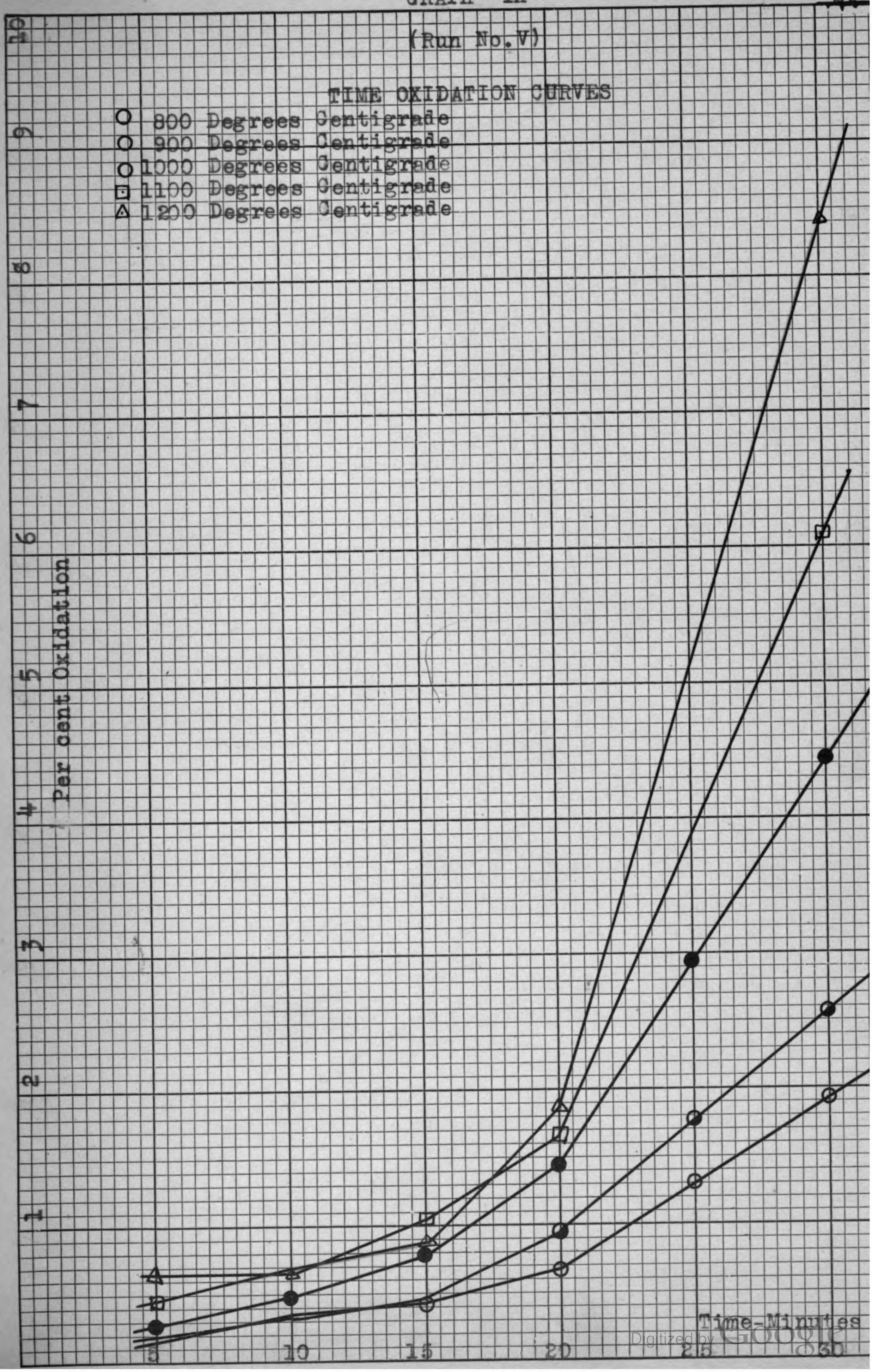

GRAPH V
(Run No.III)
TIME OXIDATION CURVES
800 Degrees Centigrade
900 Degrees Centigrade
1000 Degrees Centigrade
1100 Degrees Centigrade
1200 Degrees Centigrade
Per cent Oxidation
Time-Minu
10
9
8
7
6
5
4
3
2
1
5
10
15
20
25

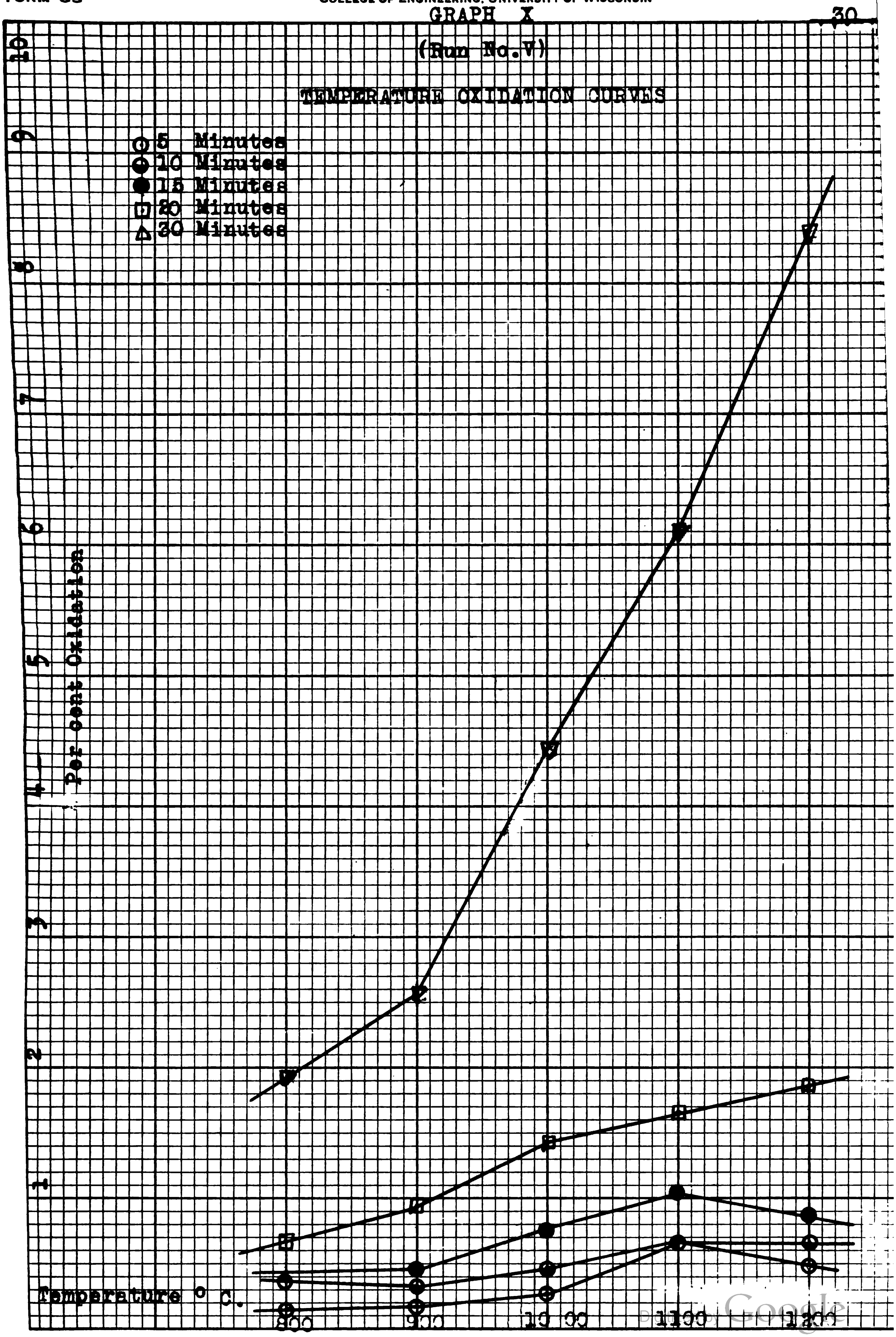

GRAPH VI
(Run No. III)
TEMPERATURE OXIDATION CURVES
5 Minutes
10 Minutes
15 Minutes
20 Minutes
30 Minutes
Per cent Oxidation
Temperature ° C.
800
900
1000
1
2
3
4
5
6
7
8
9
10

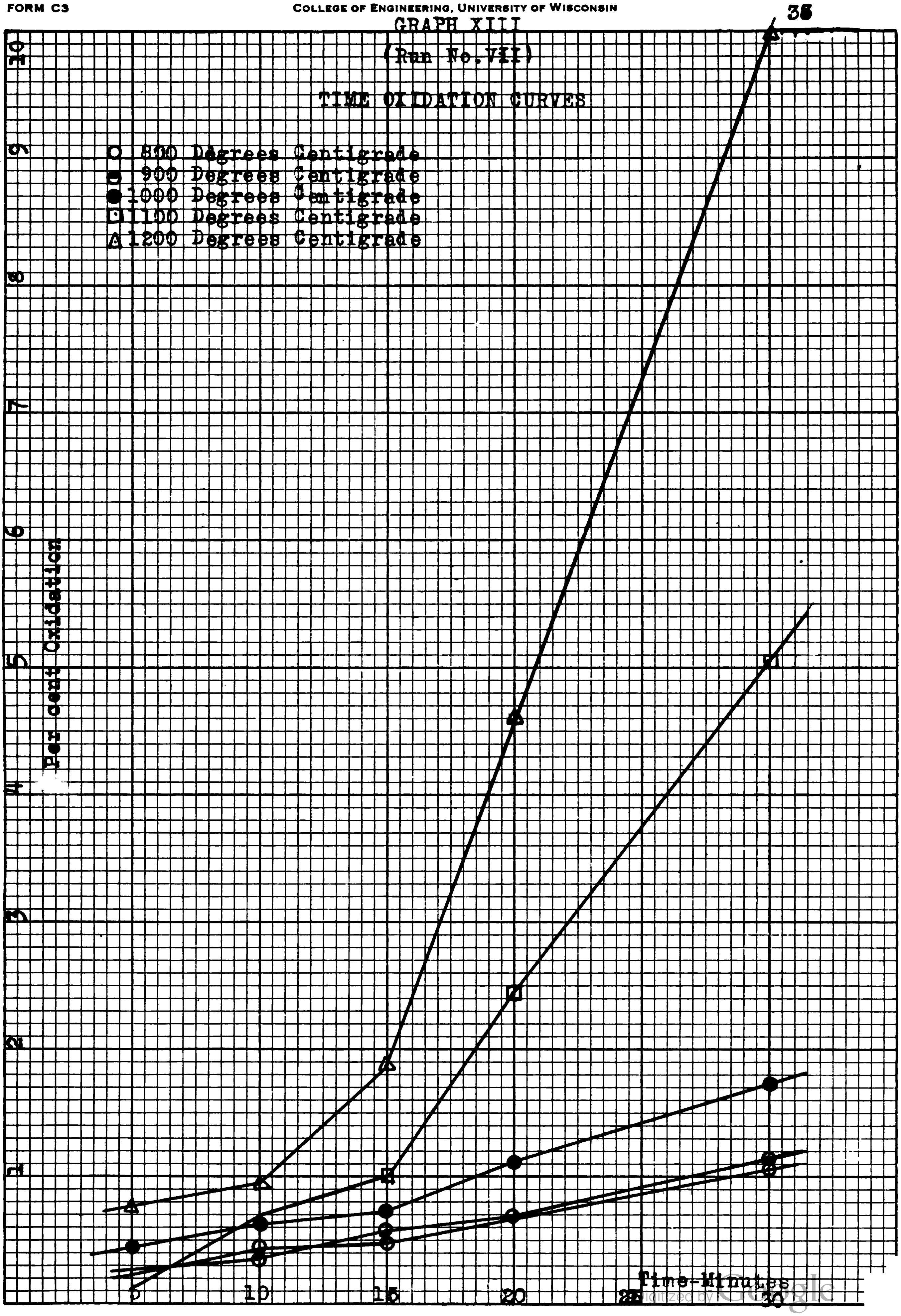

GRAPH VII
(Run No. IV)
TIME OXIDATION CURVES
800 Degrees Centigrade
900 Degrees Centigrade
1000 Degrees Centigrade
1100 Degrees Centigrade
1200 Degrees Centigrade
Per cent Oxidation
Time-Minutes
1
2
3
4
5
6
7
8
9
10
5
10
15
20
25
30

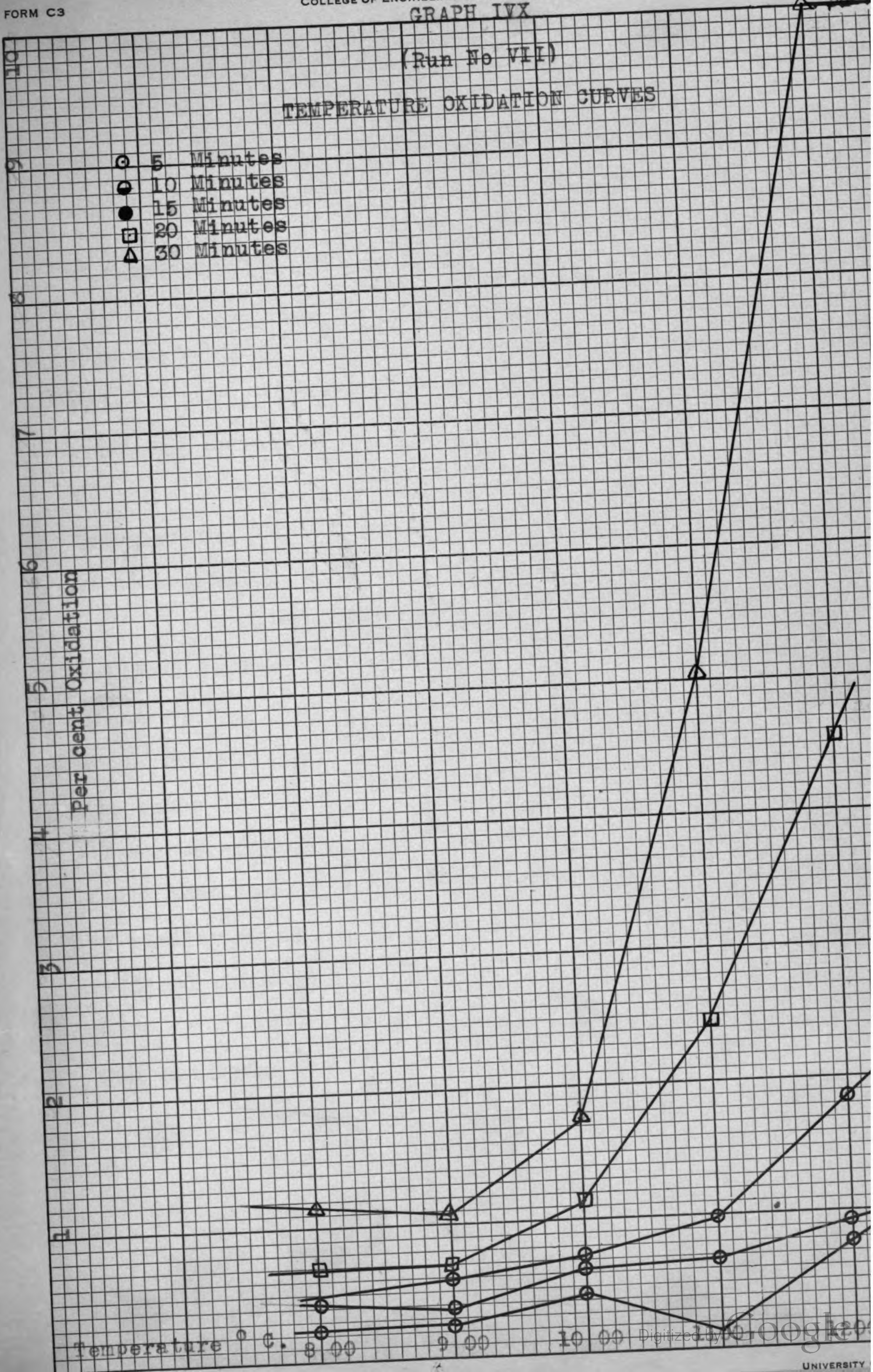

GRAPH VIII
(Run No. IV)
TEMPERATURE OXIDATION CURVES
5 Minutes
10 Minutes
15 Minutes
20 Minutes
30 Minutes
Per cent Oxidation
Temperature ° C.
800
900
1000
1
2
3
4
5
6
7
8
9
10

GRAPH IX


(Run No.V)
TIME OXIDATION CURVES
800 Degrees Centigrade
900 Degrees Centigrade
1000 Degrees Centigrade
1100 Degrees Centigrade
1200 Degrees Centigrade
Per cent Oxidation
Time-Minutes
1
2
3
4
5
6
7
8
9
10
5
10
15
20
25
30


GRAPH X
(Run No.V)
TEMPERATURE OXIDATION CURVES
5 Minutes
10 Minutes
15 Minutes
20 Minutes
30 Minutes
Per cent Oxidation
Temperature °C.
1
2
3
4
5
6
7
8
9
10
800
900
1000
1100
1200


GRAPH XIII
(Run No.VII)
TIME OXIDATION CURVES
O 800 Degrees Centigrade
900 Degrees Centigrade
1000 Degrees Centigrade
1100 Degrees Centigrade
1200 Degrees Centigrade
Per cent Oxidation
Time-Minutes
1
2
3
4
5
6
7
8
9
10
5
10
15
20
25
30


GRAPH IVX
(Run No VII)
TEMPERATURE OXIDATION CURVES
5 Minutes
10 Minutes
15 Minutes
20 Minutes
30 Minutes
Per cent Oxidation
10
9
8
7
6
5
4
3
2
1
Temperature ° C.
800
900
1000

CONCLUSIONS

1. The apparatus used facilitates rapid treatment of specimens under uniform conditions.

2. At constant temperatures the oxidation increases with the time of treatment.

3. For thirty minute periods the oxidation increases with rise of temperature.

4. For periods below thirty minutes the oxidation temperature curves indicate a marked decrease in oxidation at temperatures of 900°and 1100°C.

In cementation of steel at points above the critical temperature which in case of low carbon steel is about 900°C., carbon is very rapidly absorbed to form the gamma solution. For specimens heated to 900°C, this may be the cause for the low loss resulting, since the absorption of carbon will counter balance the loss by oxidation. The small loss occurring at 1100° may be explained on the basis of similar phenomena, in-as-much as iron shows a faint critical point at 1130°C.

5. In all runs the use of dry gas gives less oxidation than saturated gas.

6. With the use of dry gas a relative amount of

oxidation takes place during the first twenty minutes of treatment after which the oxidation increases rapidly, due probably to the free oxygen formed by the decomposition of CO_2 to O_2 and CO at temperatures above 1100° Centigrade.

7. The composition of the gas seems to have little effect on the amount of oxidation, except where the products of combustion are saturated with moisture.

8. Two specimens were treated for twenty minutes at 1000° Centigrade with a gas made up of 10% CO_2, 10% illuminating gas, 4% O_2, and 76% N_2. The resulting oxidation was 1.25% in each case, which is very much less than the corresponding oxidation in any of the runs using saturated gas. With the use of dry gas the values obtained check 1.25% very closely. The introduction of heated illuminating gas around the specimen may be a method of reducing the oxidation since the oxygen would attack the illuminating gas instead of the iron.

APPROVED BY Charles A. Mann
Instructor in Chem. Eng.

DATE June 13, 1916